THE THERMAL DECOMPOSITION OF TRIETHYLAMINE

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I wish to record my indebtedness to Professor H. Austin Taylor under whose direction this work was undertaken.

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THE THERMAL DECOMPOSITION OF TRIETHYLAMINE

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The marked similarity that has appeared up to the present in the decompositions of primary and secondary amines (3, 4, 5, 6) is significant, suggesting an explanation in the presence of the replaceable hydrogen in the amine group. The removal of this in a tertiary amine might be expected to cause a considerable change, since now the bond broken must certainly be C — N and hence data on this bond alone would be definitely available. At the same time it appeared possible that a study of the mechanism of the decomposition, hitherto neglected, might shed further light on existing difficulties in the reactions of the other amines.

The method of study again adopted was the static one, as in all previous cases, supplemented by analyses at significant points during the reaction. The triethylamine, originally an Eastman product, was stored over sodium to remove alcohol and water and distilled three times, the portion boiling between 88.7 and 90.3°C. being collected each time. The high boiling point of the amine necessitated that the capillaries and stopcocks connecting the amine reservoir, reaction vessel, and manometer be heated to prevent condensation. Since most of the measurements were made at pressures below atmospheric, a temperature of 80°C. was maintained throughout the parts of the system outside the furnace, proving sufficient for the purpose. The rate of pressure increase with time was measured at pressures from about 20 to 400 mm. at temperatures of 450, 470, 485, and 500°C.

The percentage increase in pressure for the end point of the reaction was extremely difficult to obtain, owing presumably to very slow secondary reactions occurring. Thus a sample of amine left in the system for six days at 450°C. increased in pressure 2 mm. between the sixth and seventh day. A rather arbitrary time limit was thus set at forty-eight hours at 450°C., this being reduced at the other temperatures studied by an amount in accordance with the observed temperature coefficient. In this way the pressure increase was found to vary from 200 to 250 per cent for the initial

pressure range 350 to 20 mm. These values, however, were uninfluenced by temperature, as table 1 will show.

Data for the individual experiments are most conveniently given as the times necessary for the pressure to increase by 25, 50, 75, 100, and 175 per cent of its initial value. At the lowest temperatures the times corresponding to the latter were not measured at all pressures and are therefore not listed in table 2.

The above values, especially those for 25 and 50 per cent pressure increase, being constant above about 150 mm. at 450°C., about 120 mm. at 470°C., about 50 mm. at 485°C., and at all pressures studied at 500°C. suggest that the reaction is of the first order, passing towards the bimolecular range at pressures below the limits stated.

TABLE 1

Relation between temperature and pressure increase

TEMPERATURE	INITIAL PRESSURE	PER CENT PRESSURE INCREASE
°C.	mm.	
450	25	258
450	128	221
450	242	205
470	21	256
470	317	201
485	33	254
485	286	205
500	17	268
500	161	216
500	347	194

The usual test for homogeneity of the reaction was made. The reaction vessel was packed with short lengths of Pyrex tubing sufficient to increase the surface to volume ratio a little more than seven times. Examples are given in table 3 of reactions in this packed vessel at 450°C. where no difference from the normal rates is shown.

The effect of additions of foreign gases was determined for nitrogen, ammonia, and hydrogen. The data given in table 4 were obtained.

It will be observed that experiments were made at the highest and lowest temperatures studied in each case and also at various pressures to include the effect of the added gas on the reaction in the pressure range where it appeared to have deviated from its unimolecular course. The effect of nitrogen is negligibly small at all temperatures and pressures studied. The same also applies to ammonia. Hydrogen on the other hand has a

TABLE 2

Times required for pressure to increase by certain per cent of its initial value

INITIAL PRESSURE	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
	Temperature = 500°C.				
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
15	0.25	0.56	0.91	1.30	2.9
50	0.28	0.62	0.97	1.45	3.9
69	0.25	0 57	0.96	1.40	4.0
122	0.26	0.57	0.95	1.43	4.9
138	0.28	0.63	1.04	1.55	5.35
161	0.27	0.55	0.90	1.37	4.8
185	0.27	0.58	0.97	1.48	5.4
245	0.26	0.60	0.99	1.50	5.7
285	0.27	0.61	1.01	1.57	6.6
322	0.26	0.60	1.01	1.60	7.0
347	0.26	0.59	1.04	1.60	7.8
	Temperature = 485°C.				
33	0.80	1.60	2.50	3.70	4.9
36	0.74	1.53	2.39	3.40	5.0
48	0.65	1.31	2.08	3.05	4.4
50	0.55	1.22	1.95	2.95	4.1
59	0.52	1.14	1.85	2.65	7.7
92	0.50	1.12	1.90	2 85	8.7
154	0.50	1.17	1.95	2.98	10.0
197	0.50	1.11	1.94	2.96	10.0
224	0.48	1.09	1.87	2.93	9.9
258	0.50	1.16	1.97	3.10	11.9
286	0.50	1.17	2.06	3.19	12.8
358	0.53	1.20	2.12	3.32	14.5
377	0.48	1.17	2.04	3.21	14.4
	Temperature = 470°C.				
21	1.59	3.21	5.01	7.07	
29	1.44	2.78	4.40	6.88	
62	1.31	2.81	4.73	7.11	
66	1.22	2.65	4.53	6.93	
108	1.10	2.80	4.71	7.20	
130	1.03	2.55	4.45	6.78	
162	1.02	2.49	4.40	6.82	
217	1.05	2.59	4.47	6.91	
242	0.99	2.45	4.42	6.87	
297	1.03	2.57	4.46	6.89	
317	1.03	2.54	4.40	6.89	
407	1.02	2.47	4.42	6.92	

TABLE 2—*Concluded*

INITIAL PRESSURE	FRACTIONAL LIVES				
	t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
	Temperature = 450°C.				
mm.	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
25	4.0	9.0	16.0	23.2	
34	3.8	8.9	16.0	24.3	
50	3.7	8.7	14.8	22.5	
80	3.6	8.6	14.9	22.8	
102	3.3	8.2	14.5	22.5	
128	3.0	7.8	13.8	21.5	
150	2.7	6.9	12.2	18.9	
199	2.6	6.7	12 3	19.7	
242	2.8	7.4	13.5	21.3	
297	2.7	7.4	13.4	21.2	
330	2.7	7.3	13.3	21.2	
369	2.7	7.3	13.3	21.1	

marked effect. There is evidence that it accelerates the reaction slightly in its early stages both at low and at high pressures; the low pressure rate, however, is not raised to its high pressure value. Later in the reaction, as will be seen from a comparison of the times for 175 per cent increase in pressure in the presence and absence of hydrogen, the rate of pressure increase is markedly reduced and to such an extent that the pressure–time curve reaches a sharp maximum and actually decreases again slightly on continued heating. Whether the effect in the earlier stages is a true effect due to fruitful collisions cannot be said, but certainly the effect later in the reaction must be due to a hydrogenation.

To obtain the energy of activation of the reaction the logarithms of the average values of the times for 25, 50, and 75 per cent pressure increase in the high pressure range were plotted against the reciprocal of the absolute temperature. Excellent straight lines were obtained, the slopes however increasing steadily so that the energies calculated from them were 52,080 calories for 25 per cent, 55,550 calories for 50 per cent, and 57,300 calories for 75 per cent pressure increase. In itself this is sufficient indication that the reaction is complex and that the energy of activation of the earliest reaction occurring is less than 52,000 calories and would most probably be of the order of 50,000 calories. This value is higher than that found for the primary amines, namely 44,000 calories, but is in fair agreement with the value of 49,000 calories found for diethylamine.

The first attempt to obtain some idea of the products of reaction was made by interrupting a static run when only partially completed, removing the furnace from around the reaction vessel, and replacing it with liquid

air. Only fixed gases should then remain, namely methane, hydrogen, or nitrogen. Thus, 222 mm. of amine after 10 minutes at 500°C. gave enough permanent gas at liquid air temperature to yield a pressure of 17 mm. Again, 384 mm. of amine after 23 hours at 450°C. gave a residual gas pressure of 28.5 mm. Assuming the simple gas laws to hold approximately,

TABLE 3

Reaction in vessel packed with Pyrex tubing

Temperature, 450°C.

INITIAL PRESSURE	FRACTIONAL LIVES			
	t_{25}	t_{50}	t_{75}	t_{100}
mm.	*minutes*	*minutes*	*minutes*	*minutes*
346	2.8	7.2	13.3	21.7
190	2.9	7.4	13.1	20.8

TABLE 4

Effect of added foreign gases

INITIAL PRESSURE		TEMPERATURE	FRACTIONAL LIVES				
Amine	Added gas		t_{25}	t_{50}	t_{75}	t_{100}	t_{175}
mm.	*mm.*	*°C.*	*minutes*	*minutes*	*minutes*	*minutes*	*minutes*
126	100 N_2	500	0.25	0.61	0.91	1.42	4.2
80	102 N_2	500	0.30	0.64	1.02	1.50	4.4
240	155 N_2	450	2.7	6.8	12.6	21.4	
170	150 N_2	450	2.7	7.0	12.5	19.4	
146	101 N_2	450	2.7	7.2		19.6	
81	100 N_2	450	3.5	8.1	14.4	21.6	
110	124 NH_3	500	0.28	0.61	1.03	1.55	5.3
73	143 NH_3	500	0.28	0.61	1.00	1.55	5.0
214	183 NH_3	450	2.8	7.2	13.0	20.0	
24	179 NH_3	450	4.0	8.7	14.4	22.0	
214	159 H_2	500	0.25	0.56	0.95	1.50	6.8
154	151 H_2	500	0.24	0.55	0.94	1.45	5.9
96	99 H_2	500	0.27	0.57	0.97	1.47	6.2
51	153 H_2	500	0.24	0.60	0.97	1.53	7.0
51	100 H_2	500	0.27	0.57	0.95	1.43	4.8
257	102 H_2	450	2.5	6.6	11.6	18.6	
175	143 H_2	450	2.4	6.2	11.2	17.7	
25	153 H_2	450	3.6	9.4	20.7		

these figures show that the fixed gases constituted 65 and 60 per cent respectively of the initial pressures. This would indicate that only slight amounts of ammonia and unsaturated hydrocarbons were produced during the reaction. To decide this definitely about 0.2 g. of amine was sealed under its own vapor pressure at room temperature in a glass bomb and

thoroughly decomposed at 500°C. The gas remaining was then analyzed,[1] showing on the average of several determinations 58 per cent methane, 20 per cent ethane, 3 per cent ammonia, 2 per cent unsaturated hydrocarbon (bromine absorption), no hydrogen, and the residue 17 per cent nitrogen. In all such bomb experiments, owing to the high concentration of the reactant, large amounts of a tarry deposit always form—an occurrence never observed in the individual static runs.

Samples of the triethylamine were heated at 400°C. for from one to three hours to test for intermediate products early in the reaction. In the liquid which remained after heating, the presence of some primary amine was demonstrated by the Rimini test and of a hydrazine in quantity by reduction of alkaline silver nitrate. Cyanides, by the ferrocyanide and thiocyanate tests, acetonitrile by hydrolysis with hydrochloric acid, and secondary amines by the Simon test were shown to be absent. Analysis of the gas formed under these conditions showed the presence of 8 per cent ammonia, 3 per cent unsaturated hydrocarbon, less than 1 per cent of hydrogen, and the residue on combustion gave a CO_2 to H_2O ratio of 3 to 4. This would indicate the residual gas to be either propane or a mixture of methane and butane. A further sample of this gas therefore was kept in solid carbon dioxide until no further contraction in volume occurred. The uncondensed gas gave a CO_2 to H_2O ratio of 1:2.06. The condensed gas on vaporizing and combustion gave a ratio of 4:5.2. The residual hydrocarbon is then a mixture of methane and butane, the percentages of the total gas being 22 for methane and 35 for butane, leaving a residual 32 per cent of nitrogen.

Analysis shows then that butane is present in considerable quantities in the early stages of reaction. To account for this at the same time as a hydrazine the following reaction would seem to be indicated.

$$2(C_2H_5)_3N \rightarrow (C_2H_5)_2N{-}N(C_2H_5)_2 + C_4H_{10}$$

This would probably be a second-order reaction and would be followed by the decomposition of the hydrazine and also of the butane. If it is assumed that nitrogen and butane are formed by the hydrazine, the butane in turn yielding finally methane and ethane with residual carbon as always found, two molecules of amine would yield seven molecules of gaseous products corresponding to the pressure increase of 250 per cent observed. The butane decomposition, known to be relatively slow at 500°C., would account for the slow approach to the end point. If the hydrazine decomposition is relatively fast, as appears probable from the absence of any noticeable induction period, which would be expected since the initial

[1] These analyses and the subsequent tests after partial decomposition were kindly made by W. Takacs of this laboratory.

bimolecular reaction involves no volume change, then the overall reaction in the intermediate stage would correspond to two molecules of amine yielding three of butane and one of nitrogen, approximately a two for one split. Now by the analytical method of Guggenheim (1) we can judge approximately the end point towards which a reaction is heading at any stage in its course, from three readings equally separated in time. The larger the time intervals the more accurate is the result. Applying this in three cases it is found that, at 500°C. for the first two minutes of reaction, corresponding to a pressure increase of 100 per cent, the end point should be 164 per cent and for two runs at 485°C. the end point should be 150 per cent. The errors involved in this determination do not justify the acceptance of these figures as absolute, but one fact would appear certain, namely, that the reaction in its early stages is more nearly a two for one split than the three or four for one necessary to account for the observed pressure increases of between 200 and 250 per cent.

The mechanism suggested would appear so far to be satisfactory. The decomposition of the hydrazine would most probably be unimolecular, as is known to be the case for butane. The pressure increases herein measured would thus be those of a unimolecular volume increase reaction succeeding a bimolecular reaction without volume change. The relative rates of these would control the apparent order of reaction, but at a certain lower pressure the bimolecular reaction must eventually take control and the apparent order pass to more nearly two. Extremely little is known of the postulated tetraethylhydrazine, so that further speculation must be avoided.

In view of the presence of free ammonia and unsaturated hydrocarbon and in relatively larger quantities in the earlier than later stages of reaction, it would seem that some immediate decomposition of the amine into ammonia and an unsaturated hydrocarbon was occurring. The actual amounts found, however, preclude this possibility as of real significance in the major mechanism. The simultaneous presence of ammonia and unsaturated would account for the traces of primary amine found in the analyses. The effect of added ammonia, slight if any, could only be to aid such a reaction. The effect of added hydrogen, which is the more marked in the later stages of the reaction and especially on the end point, is to be accounted for by its known hydrogenation of unsaturateds formed in the butane decomposition (2).

SUMMARY

The thermal decomposition of triethylamine has been investigated over a pressure range from 15 to 400 mm. at temperatures from 450 to 500°C. The reaction is homogeneous with an energy of activation in its early stages of the order of 50,000 calories. The mechanism suggested by analysis of

intermediate products involves the formation of tetraethylhydrazine and butane with subsequent decompositions yielding chiefly methane and nitrogen.

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